

PATENT APPLICATION TRANSMITTAL LETTER
(Large Entity)

Docket No.
5475

TO THE ASSISTANT COMMISSIONER FOR PATENTS

Transmitted herewith for filing under 35 U.S.C. 111 and 37 C.F.R. 1.53 is the patent application of:

Wilhelmina Helena Maria VELTMANS

For: **PROCESS FOR THE PRODUCTION OF CRYSTALLINE ENERGETIC MATERIALS**

Enclosed are:

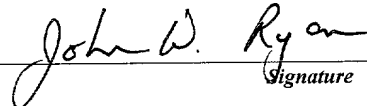
- ☐ Certificate of Mailing with Express Mail Mailing Label No.
- ☒ 7 sheets of drawings.
- ☐ A certified copy of a application.
- ☐ Declaration ☐ Signed. ☐ Unsigned.
- ☐ Power of Attorney
- ☐ Information Disclosure Statement
- ☒ Preliminary Amendment
- ☐ Other:

CLAIMS AS FILED

For	#Filed	#Allowed	#Extra	Rate	Fee
Total Claims	22	- 20 =	2	x \$18.00	\$36.00
Indep. Claims	4	- 3 =	1	x \$78.00	\$78.00
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>					\$0.00
BASIC FEE					\$690.00
TOTAL FILING FEE					\$804.00

- ☐ A check in the amount of to cover the filing fee is enclosed.
- ☐ The Commissioner is hereby authorized to charge and credit Deposit Account No. as described below. A duplicate copy of this sheet is enclosed.
 - ☐ Charge the amount of as filing fee.
 - ☐ Credit any overpayment.
 - ☐ Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.
 - ☐ Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).

Dated:


Signature

John W. Ryan, Reg. No. 33,771
DORSEY & WHITNEY LLP
1001 Pennsylvania Avenue, N.W.
Suite 300 South
Washington, D.C. 20004

cc:

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Wilhelmina Helena Maria VELTMANS

Serial No.: Unknown

Filed: Herewith

For: PROCESS FOR THE PRODUCTION OF CRYSTALLINE ENERGETIC MATERIALS

BOX: PATENT APPLICATION
Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

PRELIMINARY AMENDMENT

Prior to the examination of the above application, please amend this application as follows:

IN THE CLAIMS:

Please delete claims 3-7, and insert therefor the following claims:

8. Process according to claim 1, wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration.
9. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz;

wherein the crystallising mixture is stirred during crystallisation;

wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration.

10. Process according to claim 9, wherein the temperature during recrystallization is between 15 and 75°C.

11. Process according to claim 1, wherein the temperature during recrystallization is between 15 and 75°C.

12. Process according to claim 2, wherein the temperature during recrystallization is between 15 and 75°C.

13. Process according to claim 10, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

14. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz;

wherein the crystallising mixture is stirred during crystallisation;

wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration;

wherein the temperature during recrystallisation is between 15 and 75°C;

wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

15. Process according to claim 1, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

16. Process according to claim 2, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

17. Process according to claim 8, wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

18. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz;

wherein the crystallising mixture is stirred during crystallisation;

wherein the crystallising mixture is transported continuously through the zone of ultrasonic vibration;

wherein the temperature during recrystallisation is between 15 and 75°C;

wherein the ultrasonic vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 10 μm .

wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

19. Process according to claim 18, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

20. Process according to claim 1, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

21. Process according to claim 2, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.

22. Process according to claim 8, wherein the energetic materials are selected from the group of

explosives and high energy oxidisers.

23. Process according to claim 18, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

24. Process according to claim 19, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

25. Process according to claim 1, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

26. Process according to claim 2, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

27. Process according to claim 8, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, C120, ADN, AP, RDX, HMX and PETN.

REMARKS

The examiner is respectfully requested to consider this preliminary amendment prior to examination of the application. No new matter has been added.

Please grant any required extensions of time and charge any fees due in connection with this response to our deposit account no. 04-1425.

Respectfully submitted,

DORSEY & WHITNEY LLP.

BY: John W. Ryan
John W. Ryan
Reg. No. 33,771

Dated: March 2, 2000

Dorsey & Whitney LLP
1001 Pennsylvania Ave., NW
Suite 300 South
Washington, DC 20004
(202) 824-8800

and transport of the material. Also sensitivity determines to a large extent the governmental restrictions posed on transport and storage.

It is accordingly one object of the present invention to improve the stability of crystalline energetic materials. It is another object of the invention to improve the sensitivity, such as impact and friction sensitivity thereof.

These and other objects are realised by the present invention, which comprises a process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz. Preferably the amplitude of an ultrasonic probe used for producing the vibration is between 0.4 and 30 μm .

The present invention is based on the surprising discovery, that by carrying out the last crystallisation step in the presence of ultrasonic vibration with a frequency of between 10 and 100 kHz, the morphology, stability and sensitivity can be improved, i.e. the crystals become more rounded, the stability is better and the sensitivity is less.

In US patent No. 3,222,231 published on December 7, 1965, it is disclosed to improve the morphology of crystalline material, including ammonium perchlorate and hydrazinium nitroformate, by precipitating a solid solute out of solution, while mechanically agitating the solution and subjecting it to a high frequency vibration. According to this patent, the processing under vibration improves the morphology of the crystals. The disclosure of this patent does not indicate anything about the effect of the treatment on stability and sensitivity.

According to a more preferred embodiment the present invention is directed to an improvement in the production of hydrazinium nitroformate (HNF). HNF belongs to the class

of high energy oxidisers and can be used in high performance chlorine free solid propellants.

HNF is generally produced in crystalline form by combining hydrazine and nitroform under well defined conditions, followed by further purification using i.a. crystallisation. One method for the production of HNF is described in US patent number 5,557,015. According to this method HNF is prepared in very pure form by reacting hydrazine and nitroform in a system that is a solvent for nitroform and a non-solvent for hydrazinium nitroformate, in the presence of a proton transferring medium.

The stability of the present energetic materials, and more in particular of HNF, can be determined by vacuum thermal stability (VTS) in accordance with STANAG 4479 at 60 and 80°C for 48 to 100 hours.

The friction sensitivity is determined by BAM friction in accordance with ONU 3b)i), the impact sensitivity by BAM impact in accordance with ONU 3a)ii).

It has been noted that whereas the HNF crystals are having an aspect ratio of more than 4 after crystallisation without ultrasonic vibration, the crystals produced in accordance with the process of the present invention have an aspect ratio, which is sometimes lower than this, depending both on the applied amplitude of the ultrasonic probe and the recrystallisation method used. However, it has also been found that there is no direct link between the aspect ratio of the crystals on the one hand and the stability or sensitivity on the other hand.

The process of the present invention can be carried out in various ways. In general it is important that during crystallisation the crystallising mixture is subjected to treatment with the ultrasonic vibration. This process can be applied during crystallisation and during recrystallisation.

In case of batch processing one may subject the whole batch at the same time to an ultrasonic vibration. In

the alternative it can be done by stirring the crystallising mixture in such a way that the batch content moves through a region of ultrasonic vibration sufficiently frequently to obtain the effect. This can for example be
5 done by using an ultrasonic probe, whereby the stirring regime or the construction of the crystalliser is such that the suspension passes the vibration zone frequently. It is also possible to include the treatment in a recirculation loop of the crystalliser.

10 The temperature of the treatment is not critical, although it may have some effect on the actual stability, sensitivity and morphology. Temperatures between 0 and 100°C, preferably between 15 and 75°C can be used.

15 The present invention is now explained on the basis of the production of crystalline HNF, although it will be clear to the skilled person that other materials may be produced using the same principles, wherein variation may be applied, if necessary to take into account the actual production methods of other materials, while maintaining
20 the basic principles of the invention.

In the operation of the present invention first HNF is prepared from hydrazine and nitroform, for example as disclosed in the cited US patent No. 5.557.015, The contents of which is incorporated herein by way of
25 reference. In general this means that nitroform having a purity of more than 98.5 %, dissolved in dichloroethane, and water (6 vol.%) are mixed. At 0°C an equimolar amount of hydrazine, purity 99.5%, is added and the mixture is stirred, while keeping the temperature between 0 and 5°C.
30 The crystalline HNF obtained thereby is then subjected, either in the reaction mixture, or after crystallisation and/or additional purification, to a final (re)crystallisation in the presence of the ultrasonic vibration.

35 The invention is now further explained on the basis of a number of examples.

EXAMPLE 1 (ultrasound (US) applied during cooling-crystallisation of HNF)

5 Nitroform, dissolved in dichloroethane (23 wt.% nitroform), and water (6 vol.%) are mixed. At 0°C an equimolar amount of hydrazine, purity 99.5%, is added and the mixture is stirred, while keeping the temperature between 0 and 5°C. The crystalline HNF obtained thereby is
10 separated from the mother liquor and redissolved in methanol.

The HNF solution in methanol is subsequently cooled yielding HNF crystals. This experiment has been performed in the absence of ultrasound (US) (reference, amplitude
15 0 μm) and under ultrasonic vibration with a frequency of 20 kHz and varying ultrasonic amplitude. Figures 1, 2, 3 and 4 show the properties of HNF crystals obtained in several experiments in which the amplitude of ultrasonic vibration is varied during cooling crystallisation.

20 Figure 1 shows the positive effect of ultrasound (US) on the morphology of HNF, expressed as the Length over Diameter (L/D) and average particle size ($X_{\text{sph.}}$).

Figure 2 shows the positive effect of ultrasound (US) on the sensitivity of HNF, expressed in BAM impact and
25 BAM friction values ([N] and [N.m] respectively).

Figure 3 shows that ultrasound (US) has a positive effect on the thermal stability of HNF at 60°C. The initial gas evolution decreases in comparison to the reference sample (no ultrasound (US) = amplitude of 0 μm) and the gas
30 evolution in time decreases as well when a low amplitude of 0.4 μm is applied.

Figure 4 gives an indication of the positive effect of ultrasound (US) on thermal stability at 80°C. At 80°C the effect becomes more apparent (on the larger gas
35 evolution scale) after -80 hrs. These four figures clearly show the positive effect of ultrasound (US) during cooling

crystallisation on morphology, sensitivity and stability in comparison to the reference HNF crystallised in absence of ultrasound (US).

5 **EXAMPLE 2 (ultrasound (US) applied during drowning out crystallisation of HNF)**

HNF is prepared by the method described in example 1. The HNF in methanol solution is subsequently closed in a methylene chloride/methanol solution yielding HNF crystals. This experiment has been performed in the absence of ultrasound (US) (reference, amplitude 0 μ m) and under ultrasonic vibration with a frequency of 20 kHz and varying ultrasonic amplitude. Figures 5, 6 and 7 show the properties of HNF crystals obtained in several experiments in which the amplitude of ultrasonic vibration is varied during drowning out crystallisation.

Figure 5 shows the negative effect of ultrasound (US) on morphology; L/D increases which implies that the HNF crystals are more needle shaped.

Figures 6 and 7 show VTS results at 60 and 80°C, respectively.

From figure 6 it can be clearly seen that ultrasound (US) application reduces initial gas evolution with a minimum initial gas evolution at a low to medium ultrasound (US) amplitude (0.4-2 μ m).

Figure 7 shows that at higher temperature (80°C) the application of ultrasound (US) not only reduces the initial gas evolution but also the overall gas evolution rate in time. These three figures clearly show that in spite of the negative influence of ultrasound (US) during drowning-out crystallisation on morphology, ultrasound (US) has a positive influence on stability in comparison to the reference HNF crystallised in absence of ultrasound (US).

Claims

1. Process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10
5 and 100 kHz.
2. Process according to claim 1, wherein the crystallising mixture is stirred during crystallisation.
3. Process according to claim 1 or 2, wherein the crystallising mixture is transported continuously through
10 the zone of ultrasonic vibration.
4. Process according to claims 1-3, wherein the temperature during recrystallisation is between 15 and 75°C.
5. Process according to claims 1-4, wherein the ultrasonic
15 vibration is generated using an ultrasonic probe, the amplitude thereof being between 0.4 and 30 μm .
6. Process according to claims 1-5, wherein the energetic materials are selected from the group of explosives and high energy oxidisers.
- 20 7. Process according to claim 6, wherein the said energetic materials are selected from the group consisting of hydrazinium nitroformate, Cl_2O , ADN, AP, RDX, HMX and PETN.

	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2
--	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	---

4

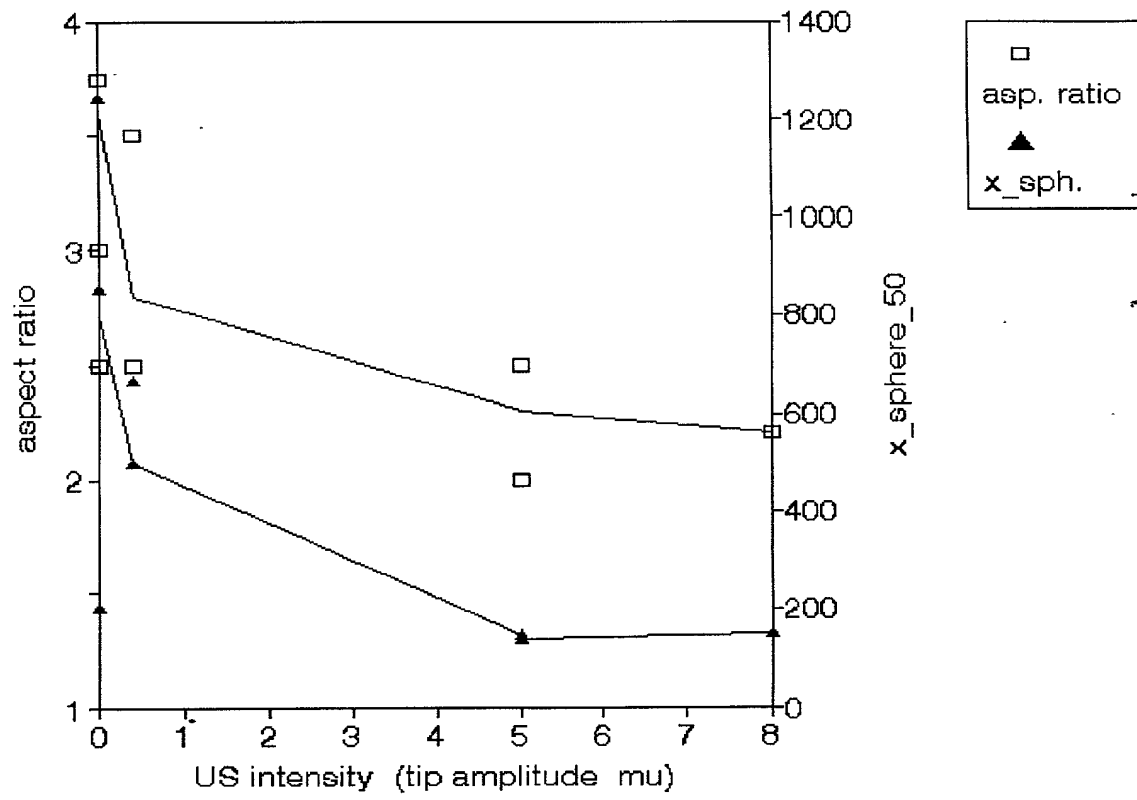


Figure 1

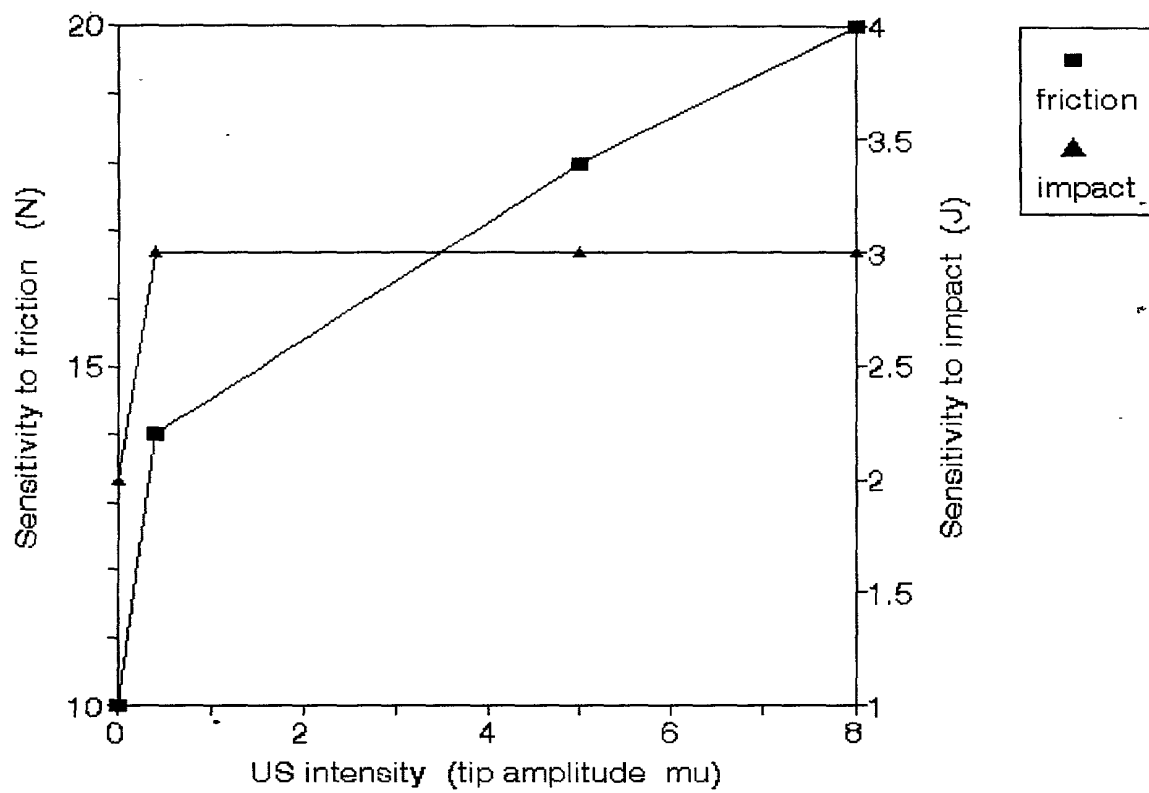


Figure 2

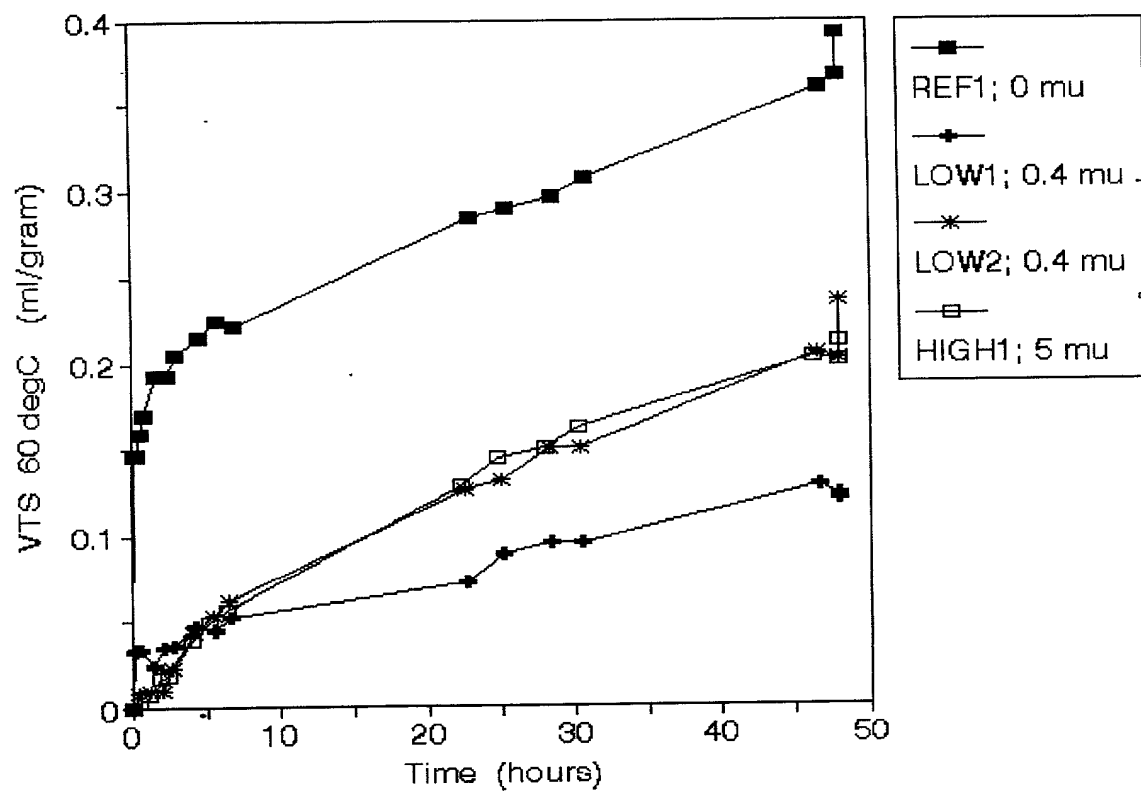


Figure 3

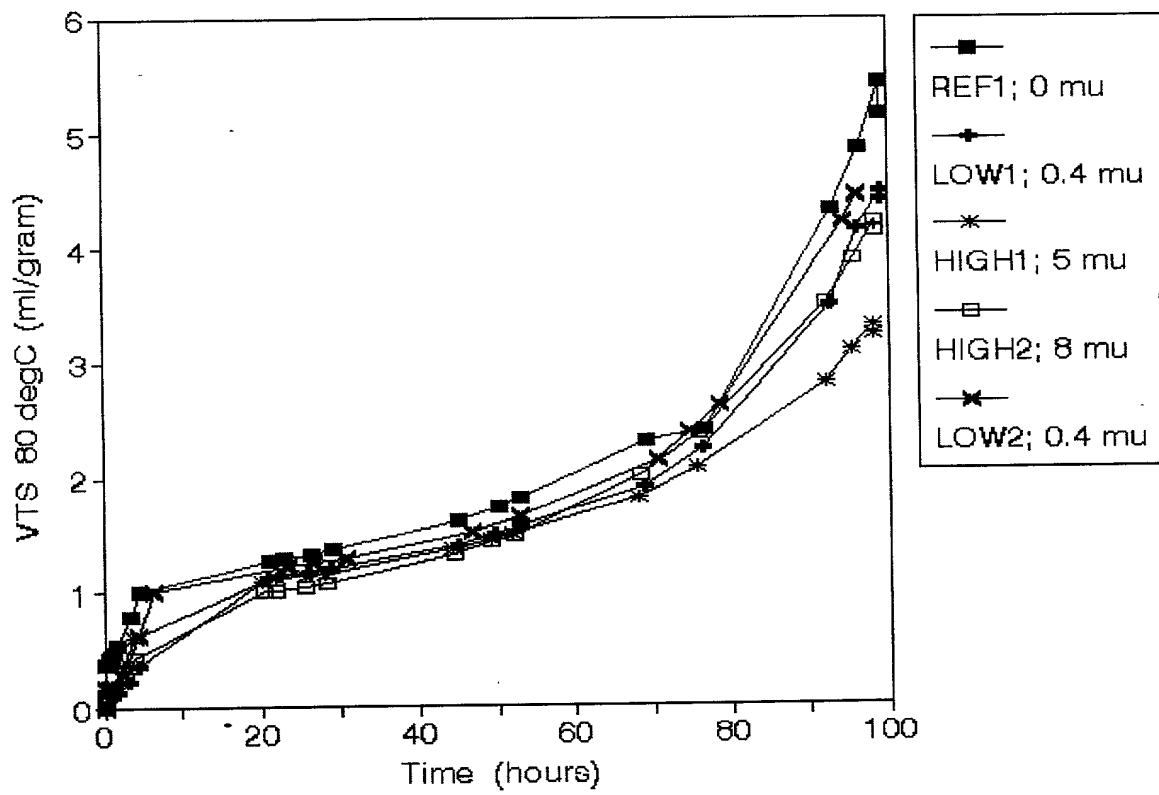


Figure 4

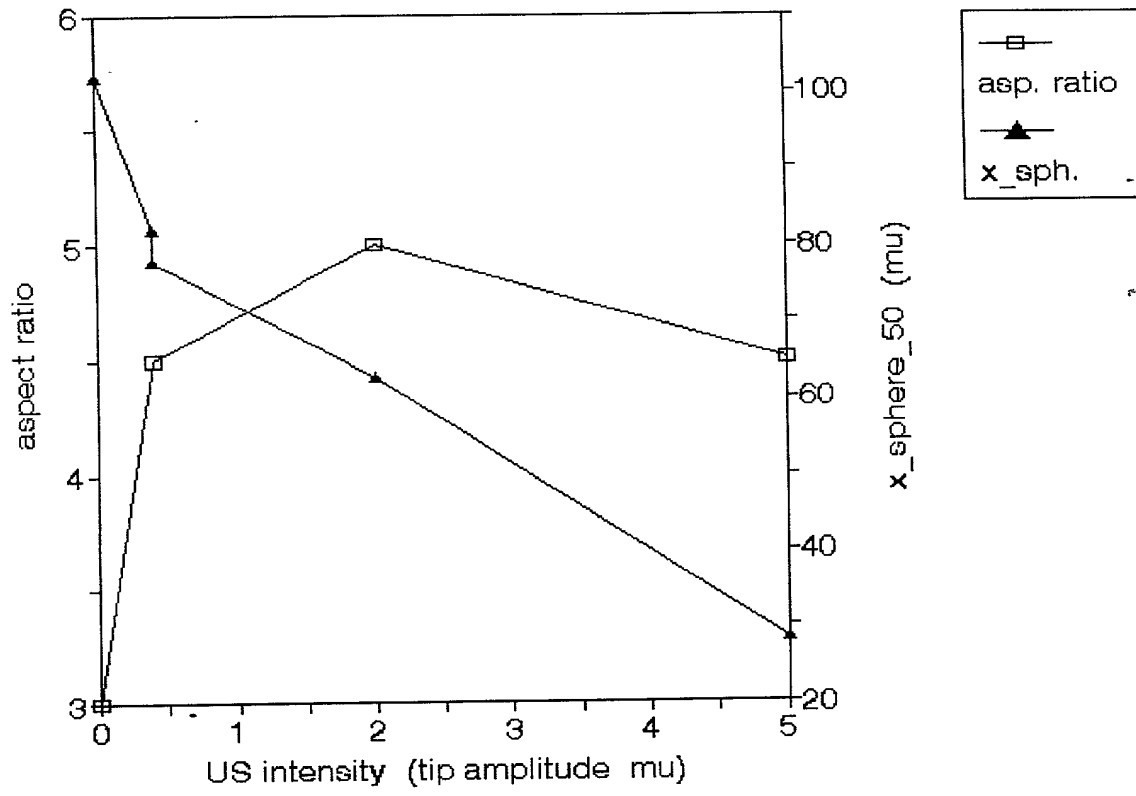


Figure 5

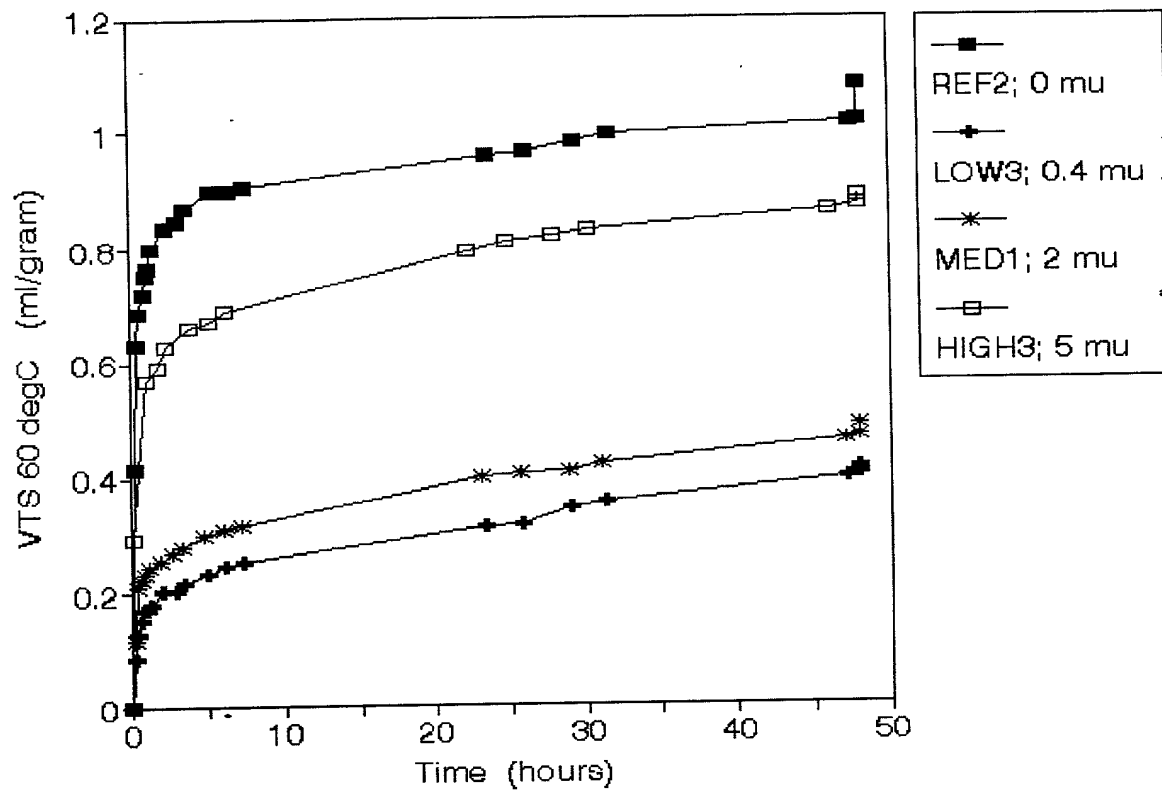


Figure 6

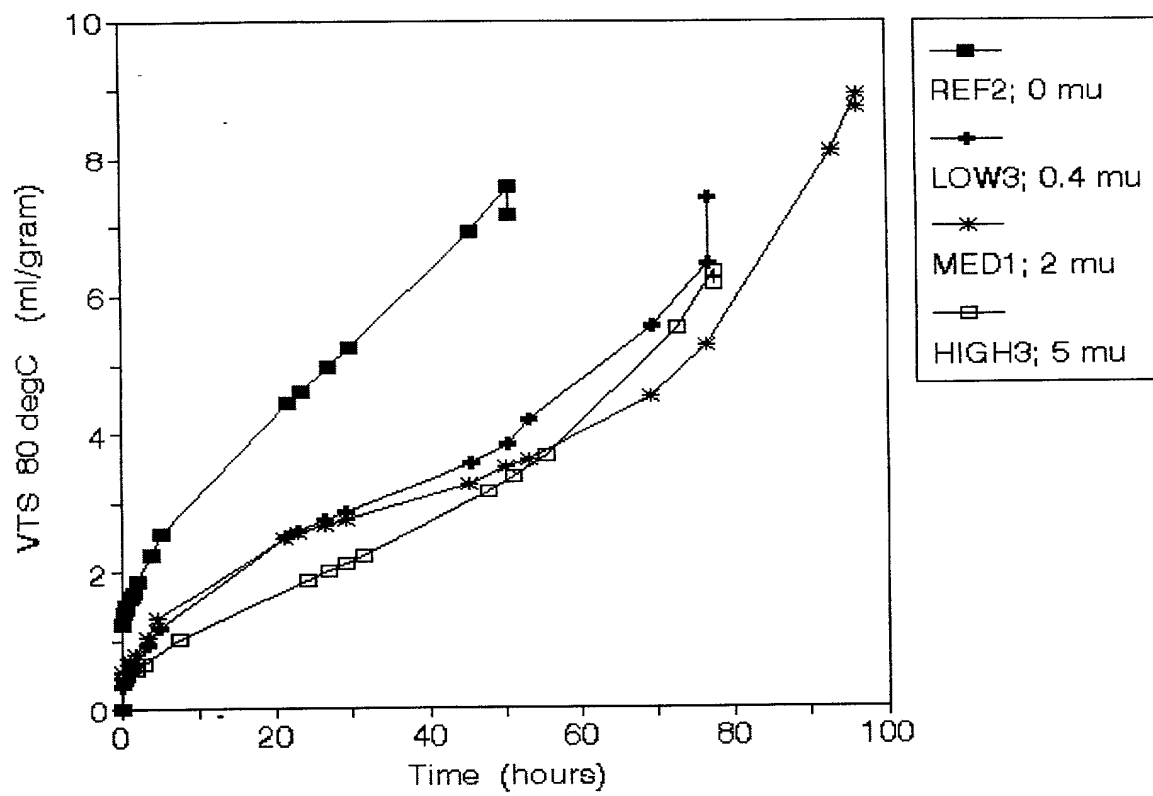


Figure 7